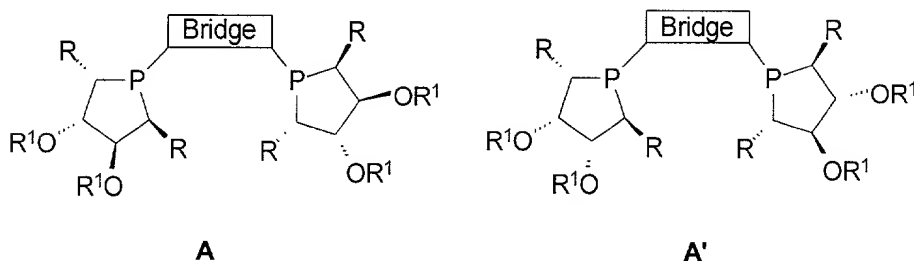


WHAT IS CLAIMED IS:

1. A compound of formula A, A', C and C', or the corresponding enantiomer:



wherein:

- a) R and R² are independently aryl, alkyl, alkyl aryl, aryl alkyl, or chiral oxazolino which may be substituted with carboxylic acid, alkoxy, hydroxy, alkylthio, thiol, dialkylamino, or diphenylphosphino groups;
- b) R¹ can be H, alkyl, silane, aryl, a water soluble unit, or a linked polymer chain or inorganic support; and

c) Bridge may be:

$-(CH_2)_n-$ where n is an integer ranging from 1 to 8;

$-(CH_2)_nX(CH_2)_m-$ wherein n and m are each integers, the same or different, ranging from 1 to 8, and X is O, S, NR^4 , PR^4 , AsR^4 , SbR^4 , divalent aryl, divalent fused aryl, divalent 5-membered ring heterocyclic group, or divalent fused heterocyclic group, wherein R^4 is aryl, alkyl, substituted aryl, or substituted alkyl; or 1,2-divalent phenyl, 2,2'-divalent 1,1'-biphenyl or 2,2'-divalent 1,2'-binaphthyl or ferrocene, each of which may be substituted with aryl, C1-C8 alkyl, F, Cl, Br, I, $COOR^5$, SO_3R^5 , $PO_3R^5_2$, OR^5 , SR^5 , NR^5_2 , PR^5_2 , AsR^5_2 , or SbR^5_2 ;

wherein the substitution on 1,2-divalent phenyl, the ferrocene or biaryl bridge can be independently halogen, alkyl, alkoxyl, aryl, aryloxy, nitro, amino, vinyl, substituted vinyl, alkynyl, or sulfonic acids; and

R^5 is hydrogen, C1-C8 alkyl, C1-C8 fluoroalkyl, or C1-C8 perfluoroalkyl, aryl; substituted aryl; arylalkyl; ring-substituted arylalkyl; or $CR^3_2(CR^3_2)_qX(CR^3_2)_pR^1$ wherein q and p are integers, the same or different, ranging from 1 to 8; R^3 is aryl, alkyl, substituted aryl, or substituted alkyl; and X is as defined above.

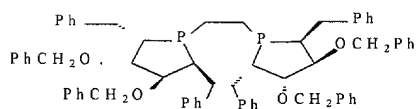
2. A compound according to claim 1, wherein the compound is of formula A or A', or the corresponding enantiomer.

3. A compound according to claim 2, wherein the compound is of formula A or A', or the corresponding enantiomer, wherein R is methyl, ethyl, or benzyl; R^1 is hydrogen or benzyl; and Bridge is:

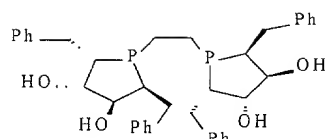
$-(CH_2)_n-$ where n is an integer ranging from 1 to 3;

1,2-divalent phenyl, 2,2'-divalent 1,1'-biphenyl, 2,2'-divalent 1,2'-binaphthyl, or ferrocene, each of which may be substituted with alkyl having 1-3 carbon atoms or OR^5 , wherein R^5 is methyl or ethyl.

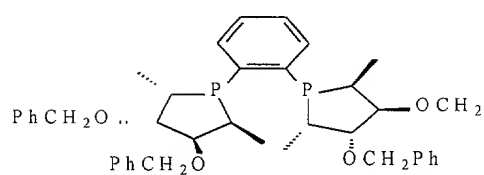
4. A compound according to claim 3, selected from L1, L3-L5, L7-L8, L10-L12, and L18-L21:



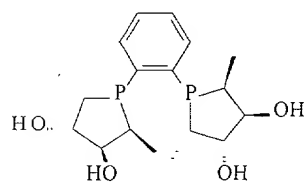
L 1 (A)



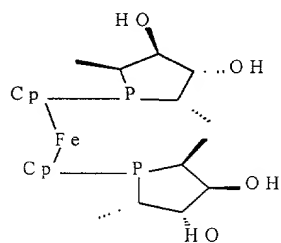
L 3 (A)



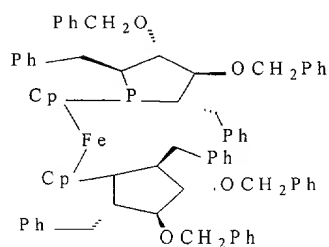
L 4 (A)



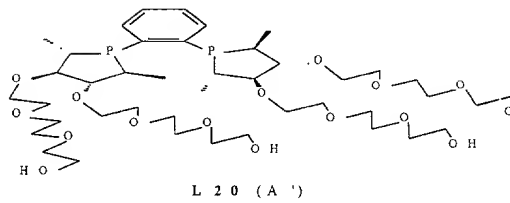
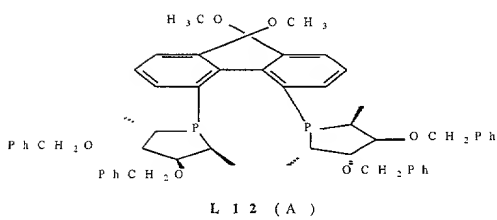
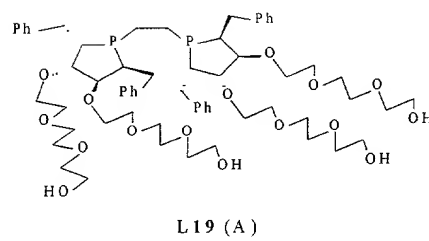
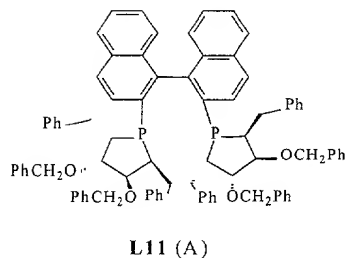
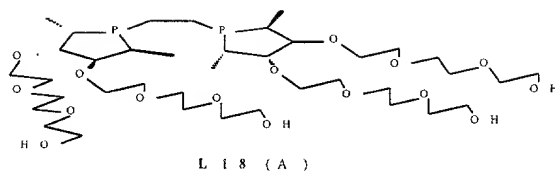
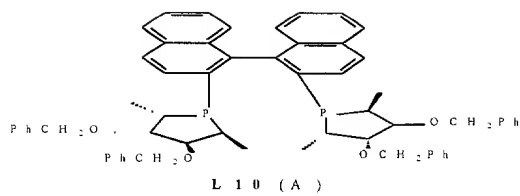
L 5 (A)



L 7 (A)



L 8 (A')





6. A compound according to claim 3, of formula 3:

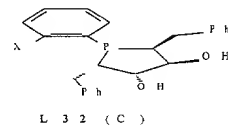
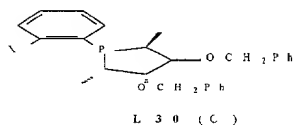
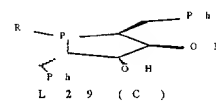
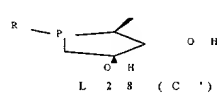
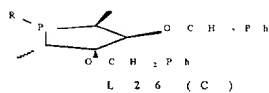


6. A compound according to claim 3, of formula 3:

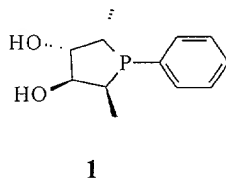


8. A compound according to claim 7, wherein R is methyl, ethyl, cyclohexyl, or phenyl; R' is hydrogen or benzyl; R² is o-X-phenyl wherein X is hydrogen or a carboxylic acid, alkoxy, hydroxy, alkylthio, thiol, dialkylamino, diphenylphosphino, or chiral oxazolino group.

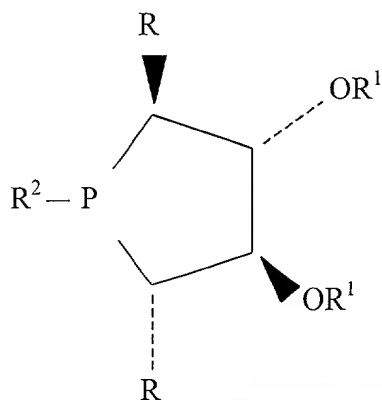
9. A compound, according to claim 1, which is selected from structures L26, L28, L29, L30 and L32, represented by the formulas:



10. A compound according to claim 1, represented by the formula (1):



11. A compound of the following formula or its corresponding enantiomer:



wherein:

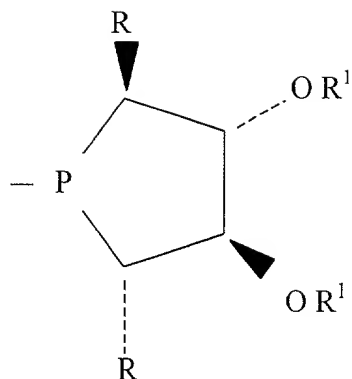
- A) R is each C₁-C₈ alkyl, C₁-C₈ alkyl aryl; aryl C₁-C₈ alkyl, aryl, each of which may be substituted with carboxylic acid, alkoxy, hydroxy, C₁-C₈ alkylthio, thiol, dialkylamino, or diphenylphosphino, or chiral oxazoline; and
- B) R¹ is each H, C₁-C₈ alkyl, silane, aryl, a water soluble unit, or a linked polymer chain or linked inorganic support; and
- C) R² is either R, H, or a symmetrical bidentate structure having the formula



wherein $\boxed{\text{BRIDGE}}$ is

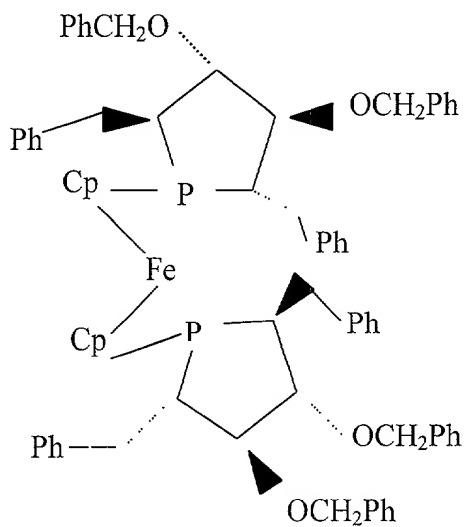
- i) $-(\text{CH}_2)_n-$ where n is an integer from 1 to 8; or
- ii) $-(\text{CH}_2)_n \text{X} (\text{CH}_2)_m-$ where n and m are the same or different integers from 1 to 8, and X is O, S, NR⁴, PR⁴, AsR⁴, SbR⁴, divalent aryl, divalent fused aryl, divalent 5-membered heterocyclic ring, or divalent fused heterocyclic ring, where R⁴ is C¹-C⁸ alkyl, aryl, substituted aryl, or substituted C₁-C₈ alkyl; or
- iii) 1, 2-divalent phenyl, 2, 2'-divalent 1, 1'-biphenyl, 2,2'-divalent, 1,1' binaphthyl, or ferrocene, each of which may be substituted independently with C₁ - C₈ alkyl or aryl, F, Cl, Br, I, COOR⁵, SO₃R⁵, PO₃R⁵₂, OR⁵, SR⁵, NR⁵₂, PR⁵₂, AsR⁵₂, SbR⁵₂, nitro, vinyl, substituted vinyl, alkynyl wherein R⁵ is H, C₁-C₈ alkyl, substituted C₁-C₈ alkyl, C₁-C₈ fluoroalkyl, C₁-C₈ perfluoroalkyl, aryl or substituted aryl; and

wherein Z is a compound selected from the group of compounds having the following formula and their corresponding enantiomers:

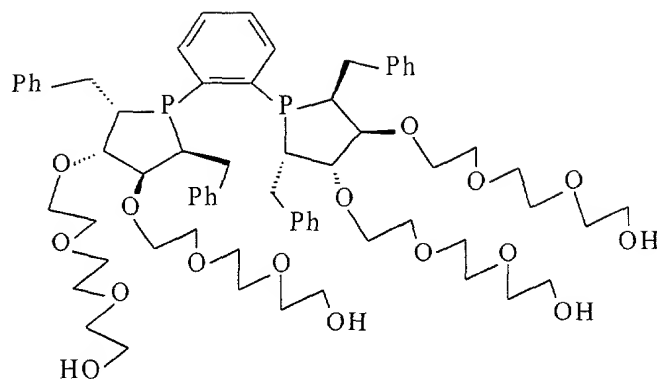


12. A compound according to claim 11 wherein R is methyl, ethyl, or benzyl; R¹ is hydrogen or benzyl, and BRIDGE is:
 $-(CH_2)_n-$ where n is an integer from 1 to 3; 1,2- divalent phenyl, 2,2' divalent 1,1' biphenyl, 2,2'-divalent 1,2' binaphthyl, or ferrocene, each of which may substituted with C₁-C₃ alkyl or OR⁵, wherein R⁵ is methyl or ethyl.

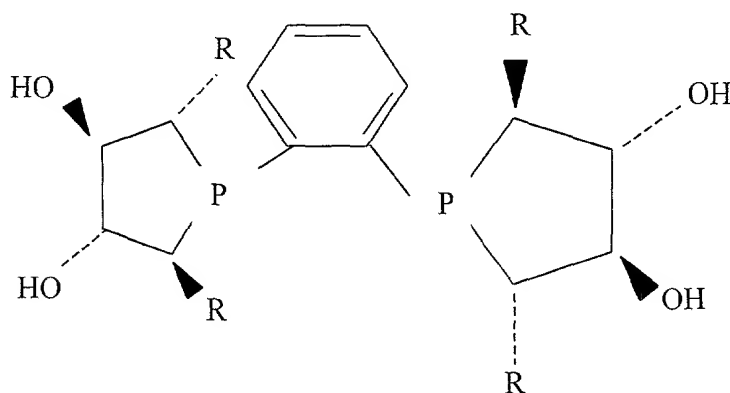
13. A compound according to claim 11 selected from the group of compounds of the following formulas and their corresponding enantiomers:



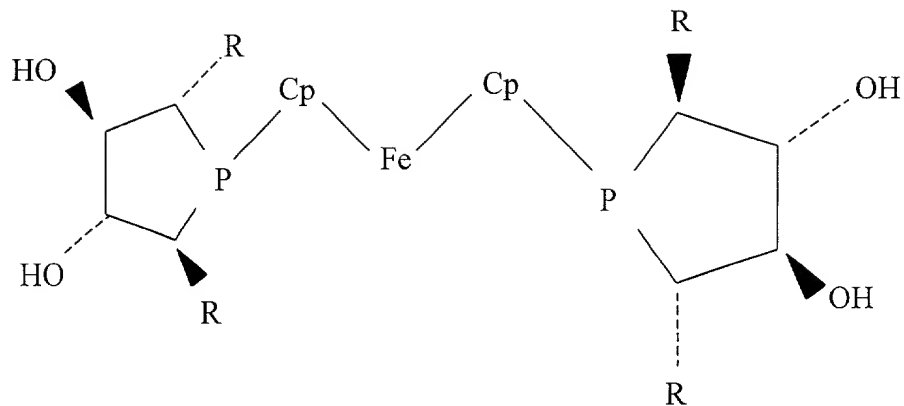
L8 (A')

**L21 (A)**

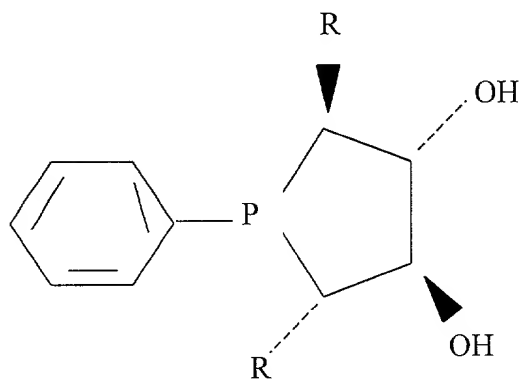
14. A compound according to claim 11 selected from the group of compounds of the following formulas and their corresponding enantiomers wherein R is either methyl or ethyl:



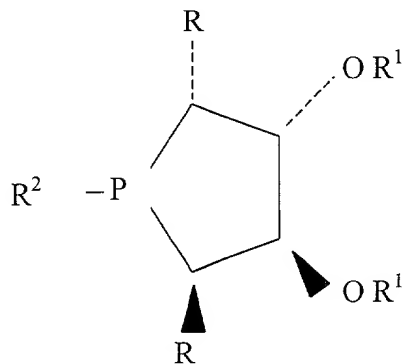
15. A compound according to claim 11 selected from the group of compounds of the following formulas and their corresponding enantiomers wherein R is either methyl or ethyl:



16. A compound according to claim 11 selected from the group of compounds of the following formula and their corresponding enantiomers:



17. A compound selected from the group of compounds of the following formula:



wherein

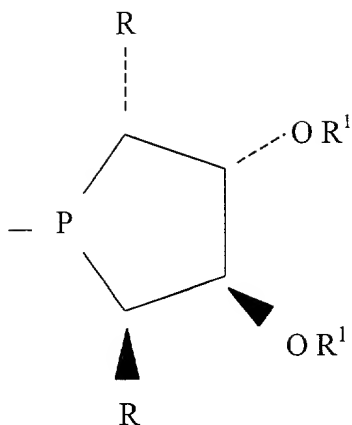
- A) R is C₁-C₈ alkyl, C₁-C₈ alkyl aryl, aryl C₁-C₈ alkyl, or aryl, each of which may be substituted with carboxylic acid, alkoxy, hydroxy, alkylthio, thiol, dialkylamino, diphenylphosphino or chiral oxazoline; and
- B) R¹ is H, C₁-C₈ alkyl, silane, aryl, a water soluble unit, or a linked polymer chain, or linked inorganic support; and
- C) R² is either R, H, or a symmetrical bidentate structure having the following formula:



wherein $\boxed{\text{BRIDGE}}$ is

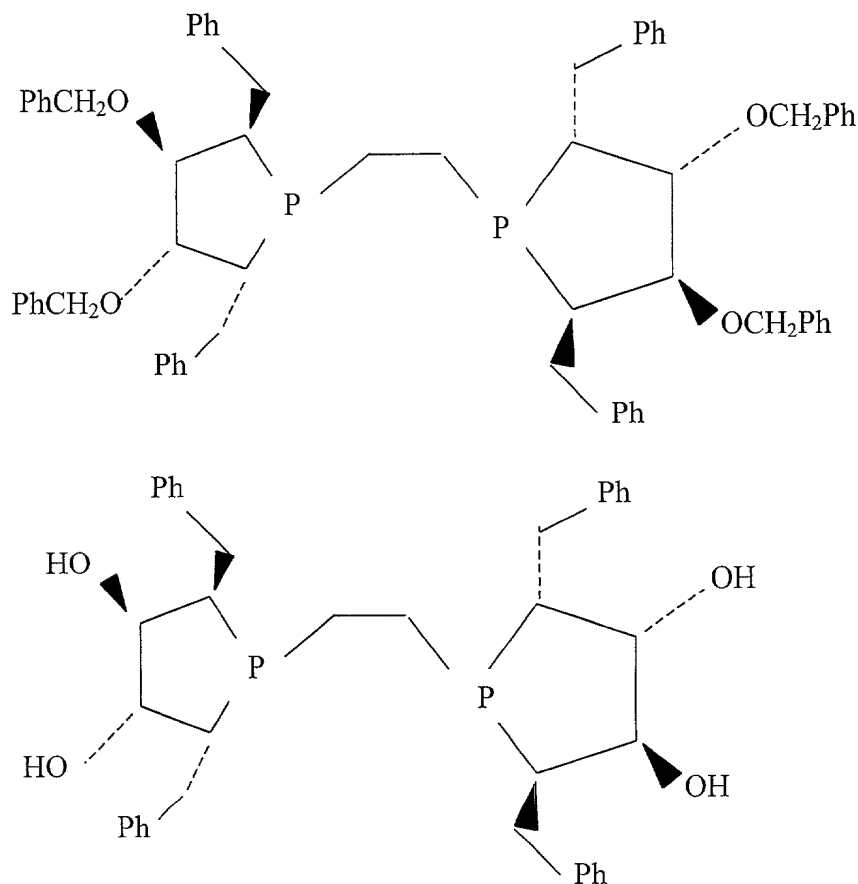
- i) $-(\text{CH}_2)_n-$ where n is an integer from 1 to 8; or
- ii) $-(\text{CH}_2)_n \text{X} (\text{CH}_2)_m-$ where n and m are the same or different integers from 1 to 8, and X is O, S, NR⁴, PR⁴, AsR⁴, SbR⁴, divalent aryl, divalent fused aryl, divalent 5-membered heterocyclic ring, or divalent fused heterocyclic ring, where R⁴ is C¹-C⁸ alkyl, aryl, substituted aryl, or substituted alkyl; or
- iii) 1, 2-divalent phenyl, 2, 2'-divalent 1, 1'-biphenyl, 2,2'-divalent, 1,1'-binaphthyl, or ferrocene, each of which may be substituted independently with C₁ - C₈ alkyl or aryl, F, Cl, Br, I, COOR⁵, SO₃R⁵, PO₃R⁵₂, OR⁵, SR⁵, NR⁵₂, PR⁵₂, AsR⁵₂, SbR⁵₂, nitro, vinyl, substituted vinyl, alkynyl wherein R⁵ is H, C₁-C₈ alkyl, substituted C₁-C₈ alkyl, C₁-C₈ fluoroalkyl, C₁-C₈ perfluoroalkyl, aryl or substituted aryl; and

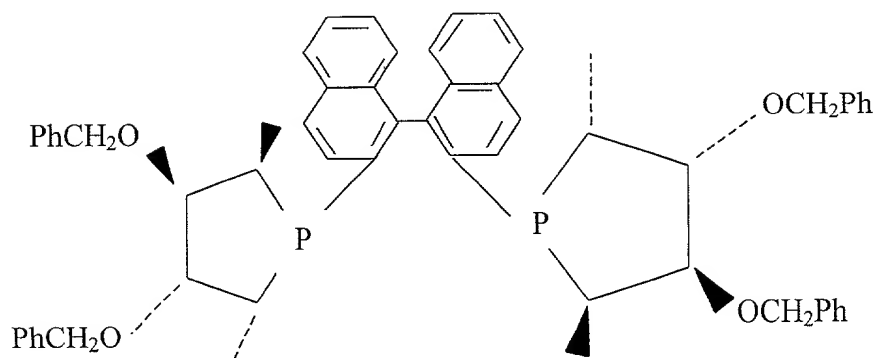
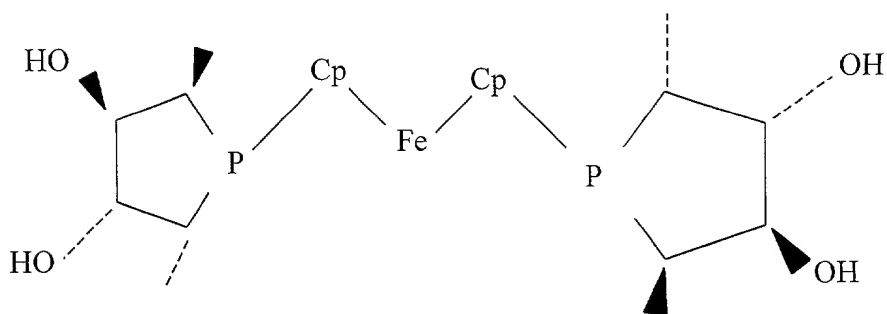
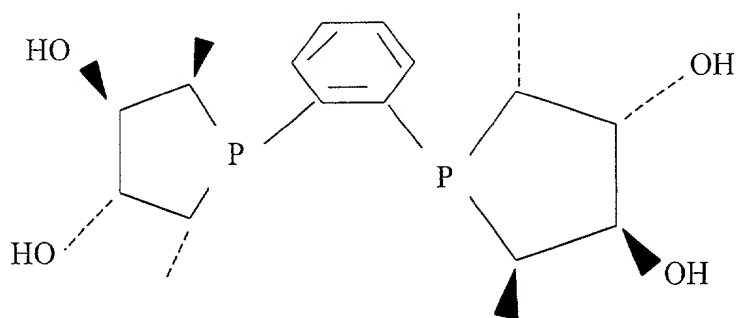
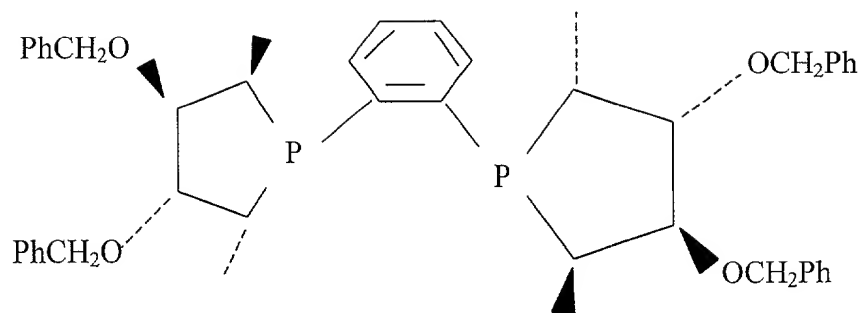
wherein Z is a compound selected from the group of compounds having the following formula:

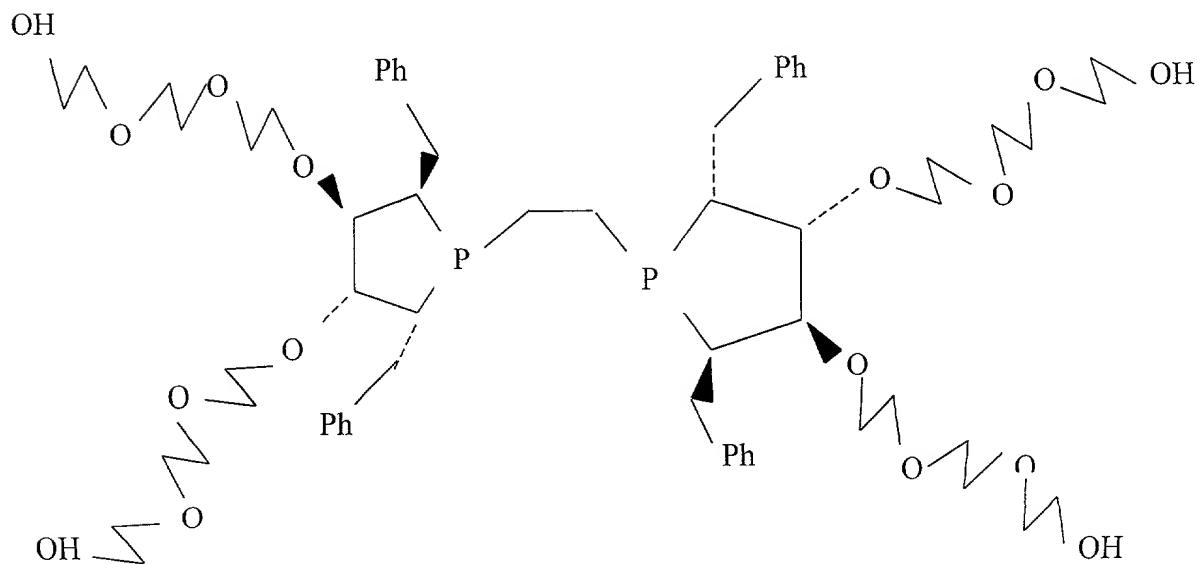
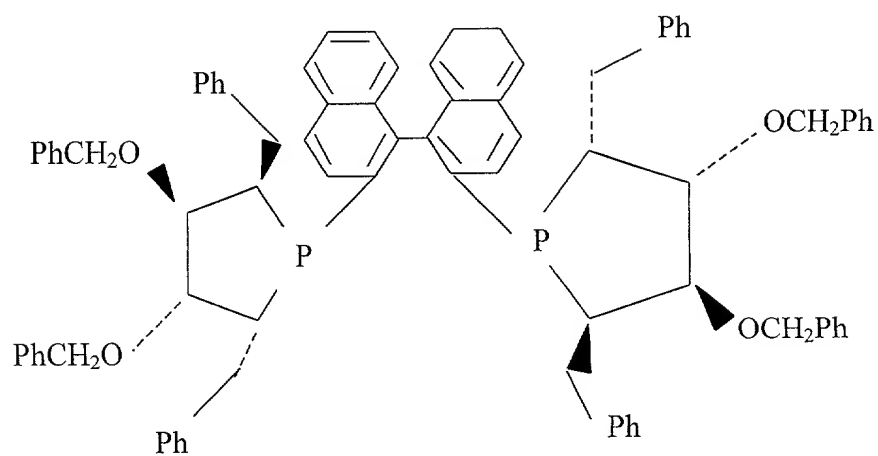
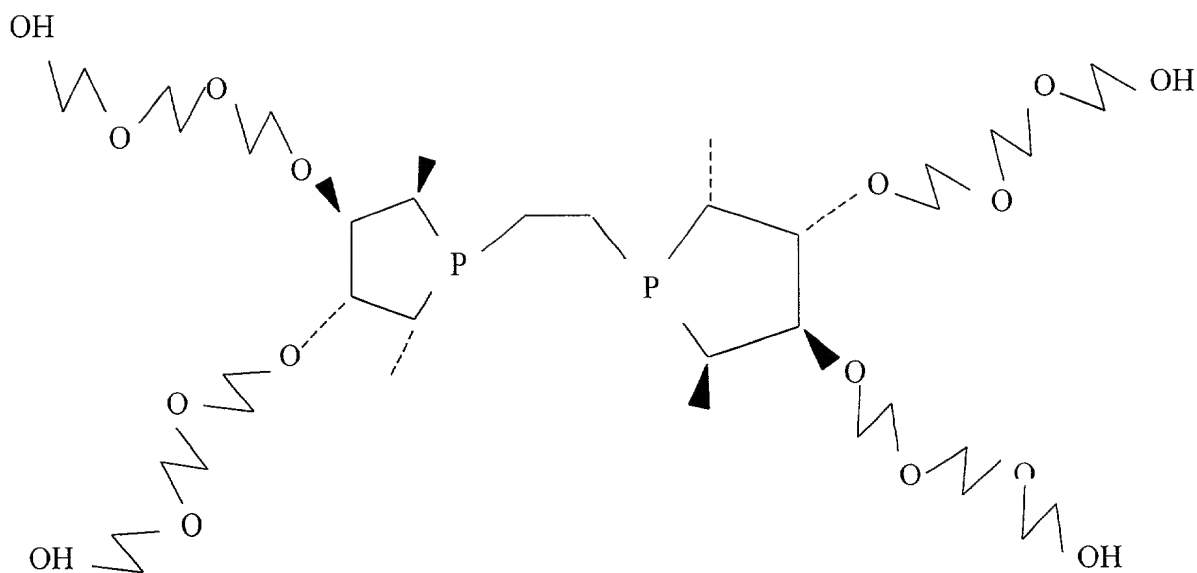


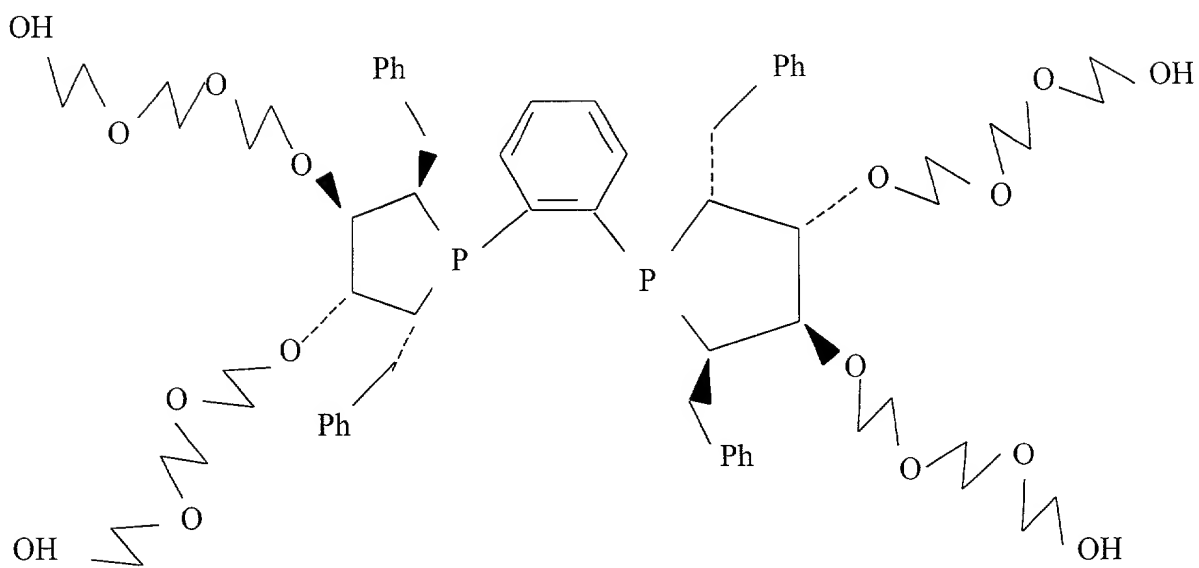
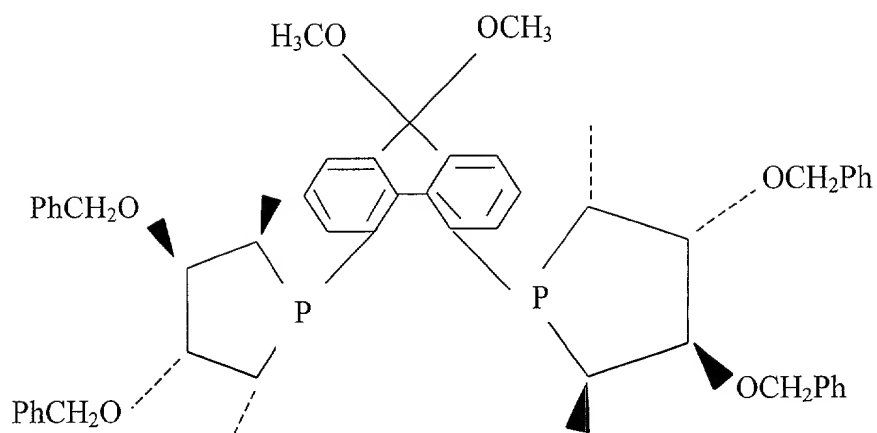
18. A compound according to claim 17 wherein R is methyl, ethyl, or benzyl; R¹ is hydrogen or benzyl; and the BRIDGE of R² is:-(CH₂)_n- where n is an integer ranging from 1 to 3; 1,2- divalent phenyl, 2,2'- divalent 1,1' biphenyl, 2,2'-divalent 1,2' binaphthyl, or ferrocene, each of which may be substituted with C₁-C₃ alkyl or OR⁵, wherein R⁵ is methyl or ethyl.

19. A compound according to claim 18 selected from the following formulas:

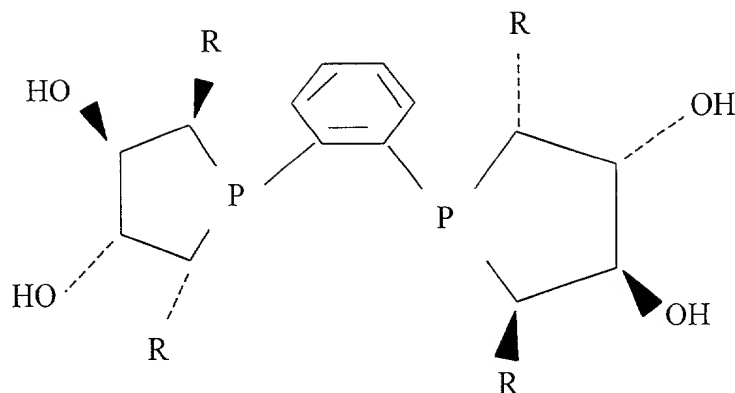




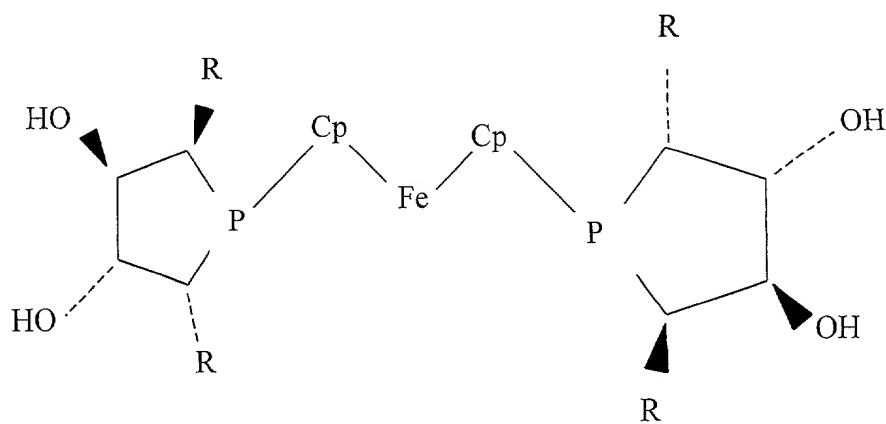




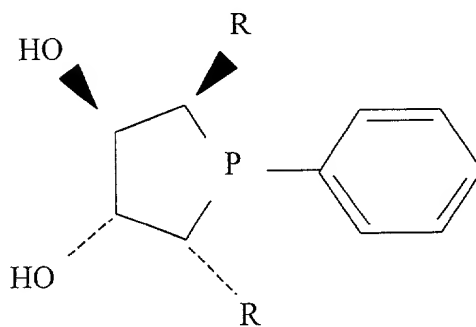
20. A compound according to claim 17 selected from the group of compounds of the following formula wherein R is methyl or ethyl:



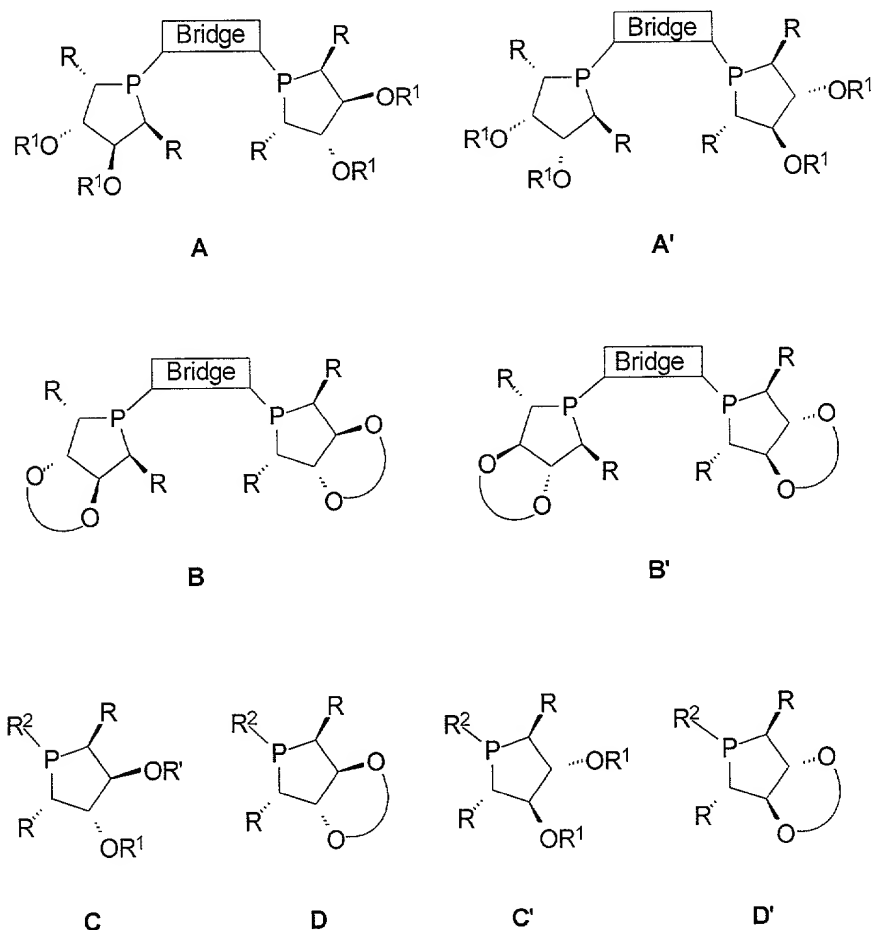
21. A compound according to claim 17 selected from the group of compounds of the following formula and their corresponding enantiomers wherein R is either methyl or ethyl:



22. A compound according to claim 17 selected from the group of compounds of the following formula wherein R is either methyl or ethyl:



23. A catalyst comprising a compound in the form of a complex with a transition metal wherein said compound is selected from compounds represented by the formula:



24. A catalyst according to claim 23, wherein the transition metal is rhodium, iridium, ruthenium, nickel, or palladium.

25. A catalyst according to claim 24, wherein said compound is a complex with a compound selected from the group consisting of: $\text{Pd}_2(\text{DBA})_3$, $\text{Pd}(\text{OAc})_2$;

$[\text{Rh}(\text{COD})\text{Cl}]_2$, $[\text{Rh}(\text{COD})_2]\text{X}$, $\text{Rh}(\text{acac})(\text{CO})_2$, $\text{RuCl}_2(\text{COD})$, $\text{Ru}(\text{COD})(\text{methylallyl})_2$, $\text{Ru}(\text{Ar})\text{Cl}_2$, wherein Ar is an aryl group, unsubstituted or substituted with an alkyl group; $[\text{Ir}(\text{COD})\text{Cl}]_2$, $[\text{Ir}(\text{COD})_2]\text{X}$; and $\text{Ni}(\text{allyl})\text{X}$; wherein X is a counterion.

26. A catalyst according to claim 25, wherein X is selected from the group consisting of: F^- , Cl^- , Br^- , I^- , BF_4^- , ClO_4^- , SbF_6^- , CF_3SO_3^- , and PF_6^- .

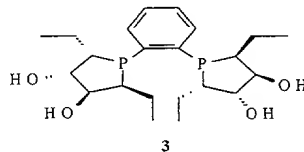
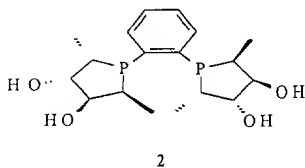
27. A catalyst according to claim 26 wherein X is PF_6^- .

28. A catalyst according to claim 24 wherein the transition metal is Ru or Rh.

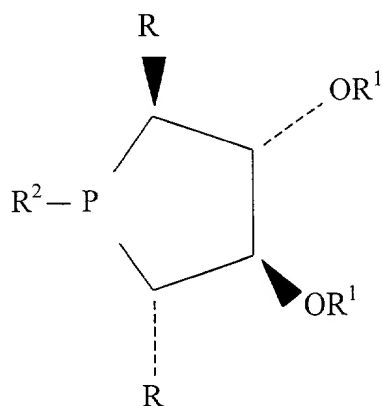
29. A catalyst according to claim 28 wherein the transition metal is Rh.

30. A catalyst according to claim 23, wherein the catalyst comprises: $\text{Ru}(\text{RCOO})_2(\text{diphosphine})$, $\text{RuX}_2(\text{diphosphine})$, $\text{Ru}(\text{methylallyl})_2(\text{diphosphine})$, $\text{Ru}(\text{aryl group})\text{X}_2(\text{diphosphine})$, $\text{Rh}(\text{RCOO})_2(\text{diphosphine})$, $\text{RhX}_2(\text{diphosphine})$, $\text{Rh}(\text{methylallyl})_2$ diphosphine, or $\text{Rh}(\text{aryl group})\text{X}_2$ (diphosphine) and X is halogen.

31. A catalyst according to claim 23 for asymmetric hydrogenation of a ketone, imine, or olefin, comprising: a complex of compounds **2** or **3** with a Rh compound selected from the group consisting of: $[\text{Rh}(\text{COD})\text{Cl}]_2$ and $[\text{Rh}(\text{COD})_2]\text{X}$, wherein X is selected from the group consisting of: BF_4^- , ClO_4^- , SbF_6^- , CF_3SO_3^- .



32. A catalyst according to claim 23 comprising a transition metal complex of a compound of the following formula or its enantiomer:



wherein:

(A) R is each C₁-C₈ alkyl, C₁-C₈ alkyl aryl; aryl C₁-C₈ alkyl, aryl, each of which may be substituted with carboxylic acid, alkoxy, hydroxy, C₁-C₈ alkylthio, thiol, dialkylamino, or diphenylphosphino, or chiral oxazoline; and

(B) R¹ is each H, C₁-C₈ alkyl, silane, aryl, a water soluble unit, or a linked polymer chain or linked inorganic support; and

(C) R² is either R, H, or a symmetrical bidentate structure having the formula

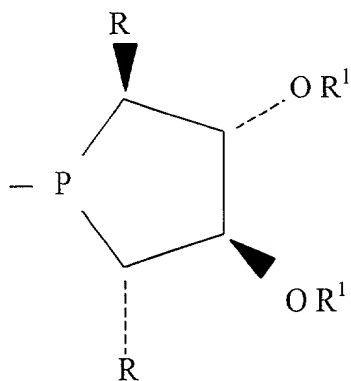


wherein $\boxed{\text{BRIDGE}}$ is

- (i) $-(\text{CH}_2)_n-$ where n is an integer from 1 to 8; or
- (ii) $-(\text{CH}_2)_n \text{X} (\text{CH}_2)_m-$ where n and m are the same or different integers from 1 to 8, and X is O, S, NR⁴, PR⁴,

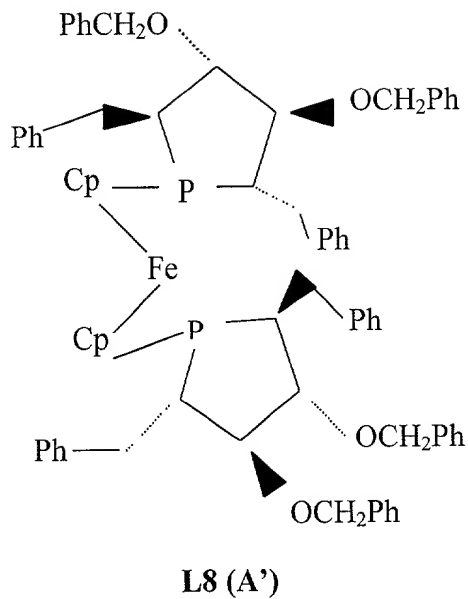
AsR⁴, SbR⁴, divalent aryl, divalent fused aryl, divalent 5-membered heterocyclic ring, or divalent fused heterocyclic ring, where R⁴ is C¹-C⁸ alkyl, aryl, substituted aryl, or substituted C₁-C₈ alkyl; or
(iii) 1, 2-divalent phenyl, 2, 2'-divalent 1, 1'-biphenyl, 2,2'-divalent, 1,1' binaphthyl, or ferrocene, each of which may be substituted independently with C₁ - C₈ alkyl or aryl, F, Cl, Br, I, COOR⁵, SO₃R⁵, PO₃R⁵₂, OR⁵, SR⁵, NR⁵₂, PR⁵₂, AsR⁵₂, SbR⁵₂, nitro, vinyl, substituted vinyl, alkynyl wherein R⁵ is H, C₁-C₈ alkyl, substituted C₁-C₈ alkyl, C₁-C₈ fluoroalkyl, C₁-C₈ perfluoroalkyl, aryl or substituted aryl; and

wherein Z is a compound selected from the group of compounds having the following formula and their corresponding enantiomers:

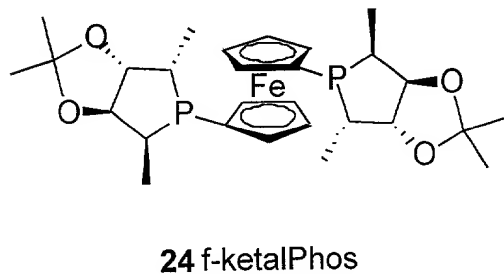


33. A catalyst according to claim 23, wherein each R¹ is independently selected from the group consisting of: methyl and ethyl groups.

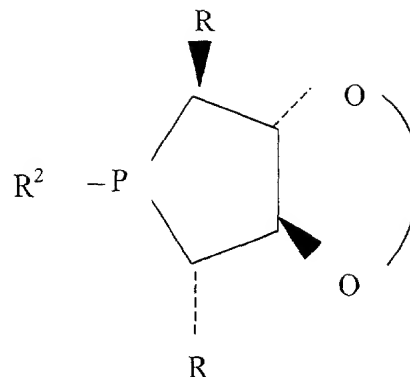
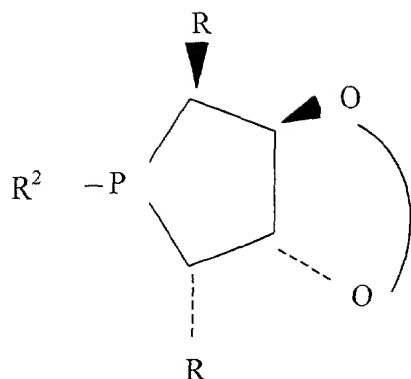
34. A catalyst according to claim 23, wherein the transition metal complex is derived from a compound of the following formula or its enantiomer:




35. A catalyst according to claim 23, wherein the transition metal complex is derived from a compound of the following formula or its enantiomer:



36. A catalyst according to claim 23 comprising a transition metal complex of a compound of the following formula or its enantiomer:



wherein

- A) R is C₁-C₈ alkyl, C₁-C₈ alkyl aryl, aryl C₁-C₈ alkyl, aryl, each of which may be substituted with carboxylic acid, alkoxy, hydroxy, alkylthio, thiol, dialkylamino, diphenylphosphino or chiral oxazoline; and
- B) the ring component  represents a protected diol, a crown ether linkage, -O-C₁-C₈ alkyl-O- wherein the alkyl group is linked to a polymer, -O-(CH₂CH₂)_n-O- wherein n is an integer ranging from 1 to 8 and the methylene groups are optionally substituted by C₁-C₈ alkyl, or O-W-O, where W is BR⁹, POR⁹, PO (OR⁹), SO₂, CO, or Si(R⁹)₂;

where R⁹ is C₁-C₈ alkyl, aryl, C₁-C₈ alkyl aryl, or aryl C₁-C₈ alkyl, alkoxy, hydroxy, alkylthio, thio, alkylamino, dialkylamino; and

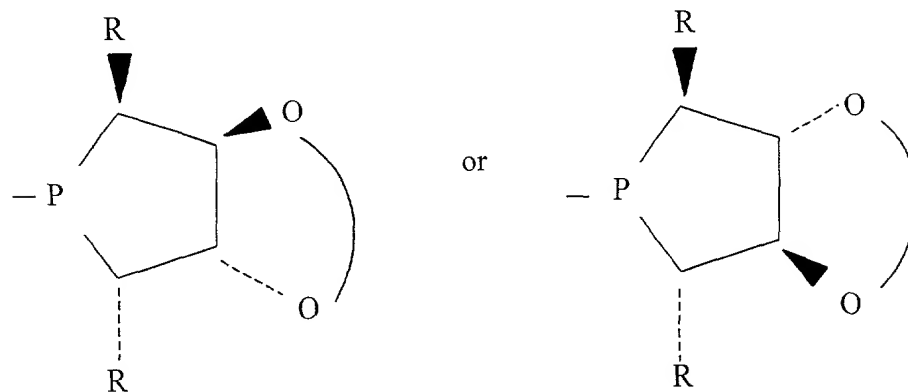
- C) R² is either R, H, phenyl or a symmetrical bidentate structure having the formula



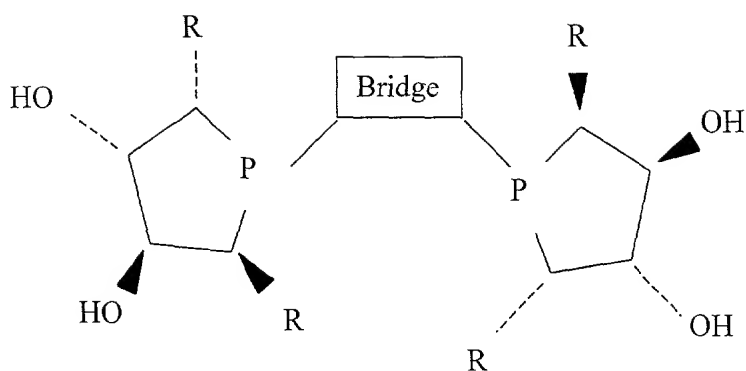
wherein $\boxed{\text{BRIDGE}}$ is

- i) $-(CH_2)_n-$ where n is an integer from 1 to 8; or
- ii) $-(CH_2)_n X (CH_2)_m-$ where n and m are the same or different integers from 1 to 8, and X is O, S, NR^4 , PR^4 , AsR^4 , SbR^4 , divalent aryl, divalent fused aryl, divalent 5-membered heterocyclic ring, or divalent fused heterocyclic ring, where R^4 is C^1 - C^8 alkyl, aryl, substituted aryl, or substituted alkyl; or
- iii) 1, 2-divalent phenyl, 2, 2'-divalent 1, 1'-biphenyl, 2, 2'-divalent, 1, 1' binaphthyl, or ferrocene, each of which may be substituted independently with $C_1 - C_8$ alkyl or aryl, F, Cl, Br, I, $COOR^5$, SO_3R^5 , $PO_3R^5_2$, OR^5 , SR^5 , NR^5_2 , PR^5_2 , AsR^5_2 , SbR^5_2 , nitro, vinyl, substituted vinyl, alkynyl wherein R^5 is H, C_1 - C_8 alkyl, substituted C_1 - C_8 alkyl, C_1 - C_8 fluoroalkyl, C_1 - C_8 perfluoroalkyl, aryl or substituted aryl; and

wherein Z is a compound selected from the group of compounds having the following formulas and their corresponding enantiomers:



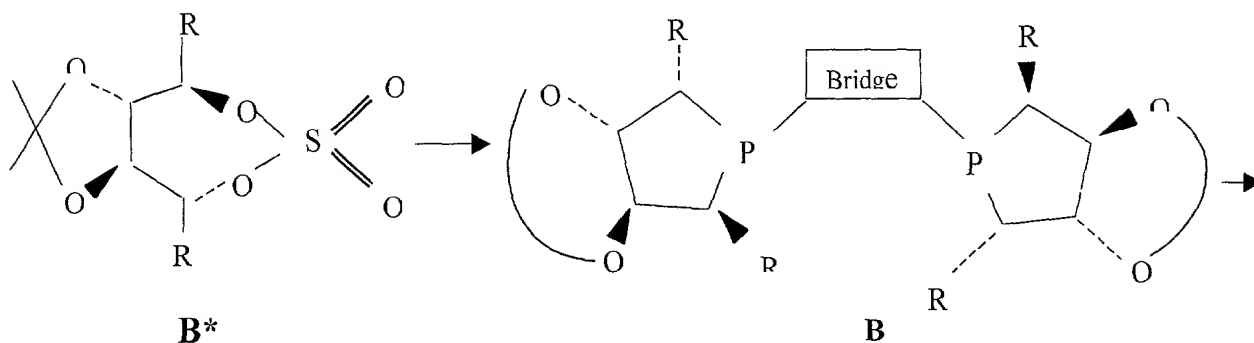
37. A process for preparing a compound of formula A, represented by the formula:



A

said process comprising:

reacting a compound of formula B* with a phosphine to form compound B:



and thereafter

reacting compound B with an acid to form compound A;

wherein the phosphine is H_2P Bridge -PH_2 ;

A) R is aryl, $\text{C}_1\text{-C}_8$ alkyl, $\text{C}_1\text{-C}_8$ alkyl aryl, or aryl $\text{C}_1\text{-C}_8$ alkyl, which may be substituted with carboxylic acid, alkoxy, hydroxy, $\text{C}_1\text{-C}_8$ alkylthio, thiol, dialkylamino, diphenylphosphino, or chiral oxazolino groups;

B) the ring component O O represents a protected diol, a crown ether linkage, or

-O-(CH₂CH₂)_n-O- wherein n is an integer ranging from 1 to 8 and the methylene groups are optionally substituted by alkyl or linked to a polymer; and

C) Bridge may be:

-(CH₂)_n- where n is an integer ranging from 1 to 8;

-(CH₂)_n-X-(CH₂)_m- wherein n, m are each integers, the same or different, ranging from 1 to 8; or

1,2-divalent phenyl, 2,2'-divalent 1,1' biphenyl or 2,2'-divalent 1,2'binaphthyl or ferrocene, each of which may be substituted with aryl or substituted aryl, or alkyl having 1-8 carbon atoms, heteroatom groups such as F, Cl, Br, I, COOR⁵, SO₃R⁵, PO₃R⁵₂, OR⁵, SR⁵, NR⁵₂, PR⁵₂, AsR⁵₂, or SbR⁵₂,

wherein the substitution on 1,2-divalent phenyl, the ferrocene or biaryl bridge can be independently halogen, C₁-C₈ alkyl, alkoxyl, aryl, aryloxy, nitro, amino, vinyl, substituted vinyl, alkynyl, or sulfonic acids; and R⁵ is hydrogen, C₁-C₈ alkyl, C₁-C₈ fluoroalkyl, or C₁-C₈ perfluoro, aryl; substituted aryl; aryl C₁-C₈ alkyl; ring-substituted arylalkyl; or CR³₂(CR³₂)_qX(CR³₂)_pR¹ wherein q and p are integers, the same or different, ranging from 1 to 8; X is O, S, NR⁴, PR⁴, AsR⁴, SbR⁴, divalent aryl, divalent fused aryl, divalent 5-membered ring heterocyclic group, or divalent fused heterocyclic group, wherein R³ and R⁴ are aryl, C₁-C₈ alkyl, substituted aryl and substituted alkyl groups.

38. A process according to claim 37 wherein:

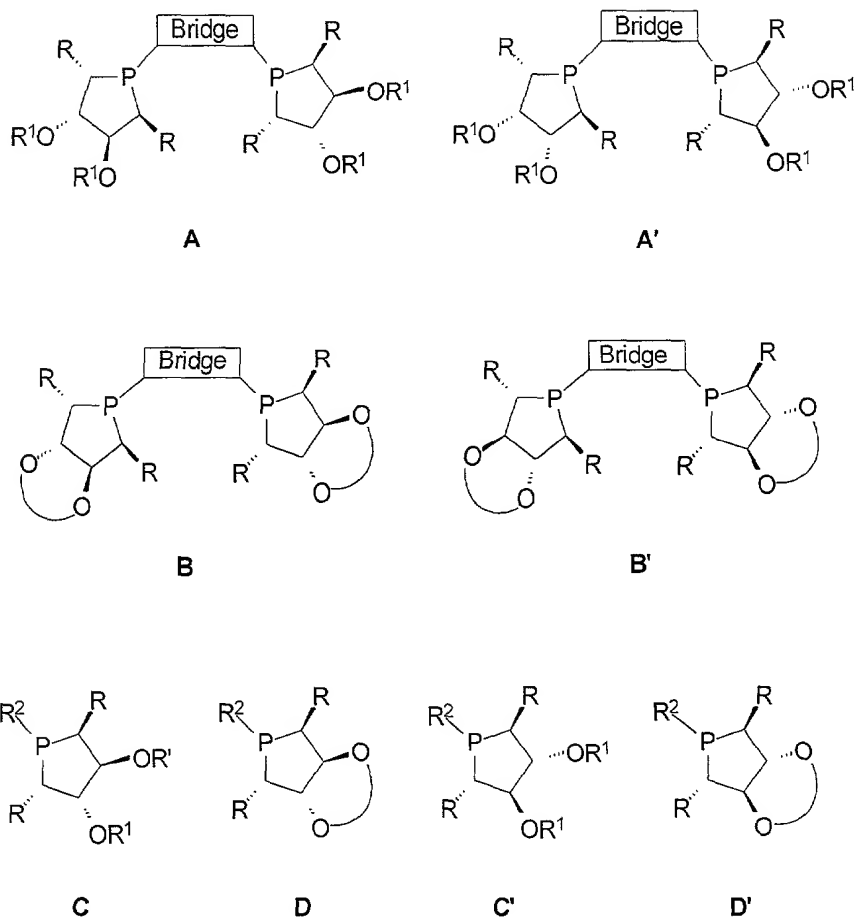
R is C₁-C₄ alkyl;

the ring component $\widehat{\text{O O}}$ represents a protected diol; and Bridge is unsubstituted or substituted 1,2-divalent phenyl.

39. A process according to claim 38 wherein R is methyl or ethyl, the ring component $\widehat{\text{O O}}$ is -O-C(CH₃)₂-O- and Bridge is unsubstituted 1,2-divalent phenyl.

40. A process comprising subjecting a substrate to an asymmetric reaction in the presence of a catalyst comprising a chiral ligand represented by the formula A,

A', B, B', C, C', D, or D', or the corresponding enantiomer:



wherein:

- R and R² are independently aryl, alkyl, alkyl aryl, aryl alkyl, or chiral oxazolino which may be substituted with carboxylic acid, alkoxy, hydroxy, alkylthio, thiol, dialkylamino, or diphenylphosphino groups;
- R¹ can be H, alkyl, silane, aryl, a water soluble unit, or a linked polymer chain or inorganic support;
- the ring component $\text{O}-\text{O}$ represents a protected diol, a crown ether linkage, -O-alkyl-O- wherein the alkyl group is linked to a polymer, or -O-(CH₂CH₂-O)_n- wherein n is an integer ranging from 1 to 8 and the methylene groups are optionally substituted by C1-C8 alkyl; and

d) Bridge may be:

$-(CH_2)_n-$ where n is an integer ranging from 1 to 8;

$-(CH_2)_nX(CH_2)_m-$ wherein n and m are each integers, the same or different, ranging from 1 to 8, and X is O, S, NR^4 , PR^4 , AsR^4 , SbR^4 , divalent aryl, divalent fused aryl, divalent 5-membered ring heterocyclic group, or divalent fused heterocyclic group, wherein R^4 is aryl, alkyl, substituted aryl, or substituted alkyl; or

1,2-divalent phenyl, 2,2'-divalent 1,1'-biphenyl or 2,2'-divalent 1,2'-binaphthyl or ferrocene, each of which may be substituted with aryl, C1-C8 alkyl, F, Cl, Br, I, $COOR^5$, SO_3R^5 , $PO_3R^5_2$, OR^5 , SR^5 , NR^5_2 , PR^5_2 , AsR^5_2 , or SbR^5_2 , wherein:

the substitution on 1,2-divalent phenyl, the ferrocene or biaryl bridge can be independently halogen, alkyl, alkoxyl, aryl, aryloxy, nitro, amino, vinyl, substituted vinyl, alkynyl, or sulfonic acids; and

R^5 is hydrogen, C1-C8 alkyl, C1-C8 fluoroalkyl, or C1-C8 perfluoroalkyl, aryl; substituted aryl; arylalkyl; ring-substituted arylalkyl; or $CR^3_2(CR^3_2)_qX(CR^3_2)_pR^1$ wherein q and p are integers, the same or different, ranging from 1 to 8; R^3 is aryl, alkyl, substituted aryl, or substituted alkyl; and X is as defined above;

wherein said asymmetric reaction is a hydrogenation, hydride transfer, hydrosilylation, hydroboration, hydrovinylation, olefin metathesis, hydroformylation, hydrocarboxylation, allylic alkylation, cyclopropanation, Diels-Alder, Aldol, Heck [m + n] cycloaddition, or Michael addition reaction.

41. A process according to claim 40, wherein said asymmetric reaction comprises asymmetric hydrogenation of a ketone, imine, enamide, or olefin.

42. A process according to claim 40, wherein said asymmetric reaction comprises Rh(I)-catalyzed hydrogenation of a dehydroamino acid or an ester thereof.